

SCIENCE FOR GLASS PRODUCTION

UDC 666.1 031

ROLE OF SODIUM SULFATE IN GLASS TECHNOLOGY

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Translated from *Steklo i Keramika*, No. 11, pp. 3 – 8, November, 2012.

Sodium sulfate is widely used as a fining agent in high-tonnage glass technology. Since the conditions for redox glassmaking and $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ equilibrium displacement are formed under the influence of sulfate, the glassmaking process and glass quality largely depend on the quality and particulars of sulfate interaction with a reducing agent. The reactions and stages of sulfate action in the batch and molten glass are examined.

Key words: sodium sulfate, oxidation, reduction, batch, glassmaking, fining, equilibrium forms of iron, acid-base properties, chemical oxygen demand, redox potential.

Sodium sulfate Na_2SO_4 is widely used in batch for making sheet, container, electrotechnical and other types of glass, predominately high-tonnage glass [1]. Its role in glassmaking is multifaceted:

- source of Na_2O and SO_3 in the glass;
- promoting the formation of low-melting eutectic at the silicate-formation stage;
- fining agent, precipitating during decomposition at high temperatures a gas phase in the form of large bubbles, which entrain via Stoke's law small bubbles ("seeds");
- oxidizer via oxygen release in the decomposition reaction $\text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$;

➤ surface-active component decreasing the surface tension at the gas-phase – molten-glass interface, which promotes dissolution of gaseous inclusions and their breakdown from the surface layer of the molten glass.

Sodium sulfate can be used as the **main source of Na_2O** (sulfate batches) or a **minor additive** in soda batch.

At present for high-tonnage glass (sheet, container and others) Na_2SO_4 is used as a **minor additive** in amounts 1 – 5%³ of the total content of alkali components of the batch.

Currently, the sulfate/soda ratio is 1 : 20, down from 1 : 6 used previously. This is dictated by the need to decrease the amount of SO_2 in the kiln gases and by the complexity of melting batches containing sulfate.

For batch with > 2% Na_2SO_4 a reducing agent is added or the glass is made in a reducing medium, since under these conditions sodium nitrate reacts with the batch components and intermediate products are formed.

There are ample works devoted to the physical-chemical processes occurring in molten glass with sodium sulfate being used and the interaction of sodium sulfate with a reducing agent during glassmaking. However, the results obtained for different glass compositions do not have a clear interpretation.

The first works on sulfate use in glassmaking belong to É. Laksman (1784, Irkutsk). He also proposed adding carbon to sulfate. O. Schott performed more detailed studies in 1871. Subsequent results are presented in a monograph by H. Jensen-Marwedel and R. Brückner [2].

Glass compositions and glassmaking conditions have changed since then. Research in this field is ongoing, since actual batch and glass compositions as well as the glassmaking conditions and redox potential (ORP) of molten glass determine the behavior of sulfate and the sulfate/carbon ratio, which affect the glassmaking process and the quality, spectral characteristics, and uniformity of glass, which in turn affects the mechanical, thermal and chemical properties of the product [3 – 6].

The requirements for uniformity and the spectral characteristics of glass are becoming increasingly more stringent. For rational utilization of raw materials individual producers are offering many proprietary brands of sulfates and reducing agents with the required content of the main substance but differing with respect to impurity content, dispersity and

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³ Here and below the content by weight, %.

moisture content. Definite technological problems arise in glass production with such sulfates [6].

Sodium sulfate does not always help in fining molten glass. At the fourth international congress on glass in Paris in 1956 A. K. Lyle reported on the effect of adding sodium sulfate to fine glass in the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$, which include sheet and container glass, as a function of the component concentrations with 0.3% SO_3 in the glass. It prolongs the fining time in glasses where silica together with Na_2O comprise $> 83\%$ ($S + 0.5N \geq 83\%$) in a wide composition range [1]. In modern float glass SiO_2 comprises 72% and Na_2O 14% ($S + 0.5N = 79\%$), i.e., float glass falls within the composition range where sodium sulfate is an effective fining agent.

Acidic glasses are characterized by lower dissolved gas content than basic glasses. A 1% increase of SiO_2 content gives a 0.03% reduction of the SO_3 in molten glass. This SO_3 content corresponds to $1.9 \text{ cm}^3 \text{ SO}_2 + \text{S}_2$ per 1 m^3 melt at 1400°C . This shows how much gas can be released as a result of a change in solubility even with a very small change in the chemical composition. The SO_3 content in molten glass decreases all the more the lower the Na_2O content.

Sodium sulfate is an effective additive not only for $\text{Na}-\text{Ca}-\text{Si}$ glasses. Sodium sulfate is known to accelerate melting for borosilicate glass [7]. At the request of one of the enterprises we replaced the expensive fining agents As_2O_3 , Sb_2O_3 and CeO_2 in combination with saltpeter for borosilicate glass with composition E were replaced with sodium sulfate; the work was done under industrial conditions [8].

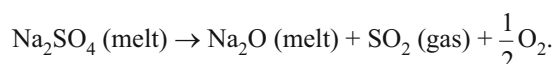
Sodium sulfate, as other agents accelerating $\text{Na}-\text{Ca}-\text{Si}$ glass making, affects the formation of low-melting eutectics and is characterized by the fact that the liquid phase appears sooner — $40 - 50^\circ\text{C}$ lower than in a purely soda batch.

Sodium sulfate in batch used for sheet and colorless container glass is characterized by specific reactions. For example, the following reactions occur in soda batch used for sodium-calcium-silicate glass:

- $\text{CaNa}_2(\text{CO}_3)_2$ formation (below 600°C);
- the reactions $\text{CaNa}_2(\text{CO}_3)_2 + 2\text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{CO}_2$ ($600 - 830^\circ\text{C}$) and $\text{Na}_2\text{CO}_3 + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{CO}_2$ ($720 - 830^\circ\text{C}$);
- eutectic and flux formation processes: $\text{CaNa}_2(\text{CO}_3)_2 - \text{Na}_2\text{CO}_3$ ($740 - 800^\circ\text{C}$);
- melting of the double carbonate $\text{CaNa}_2(\text{CO}_3)_2$ (813°C);
- melting of Na_2CO_3 (855°C).

Thus, melt (eutectic) appears in batch at a temperature below the melting temperature of soda.

The thermal decomposition of sodium sulfate proceeds follows the general scheme



The final decomposition of sulfate occurs at temperatures above 1400°C .

However, even though the melting temperature (884°C) of sulfate is comparatively low the reaction with the components of the batch at this temperature is impeded. For this reason a preliminary stage of sulfate de-oxidation by interaction with a reducing agent is introduced. Then the first processes occurring in the batch with sodium sulfate will be represented as follows:

- sulfate de-oxidation:
 $\text{Na}_2\text{SO}_4 + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2$ ($740 - 800^\circ\text{C}$);
 $\text{Na}_2\text{S} + \text{CaCO}_3 = \text{CaS} + \text{Na}_2\text{CO}_3$ ($740 - 800^\circ\text{C}$);
- eutectic formation: $\text{Na}_2\text{S} - \text{Na}_2\text{SO}_4$ (740°C);
 $\text{Na}_2\text{S} - \text{NaCO}_3$ (756°C); $\text{NaCO}_3 - \text{CaNa}_2(\text{CO}_3)_2$ (780°C);
 $\text{Na}_2\text{SO}_4 - \text{CaCO}_3$ (795°C); $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{SiO}_3$ (865°C);
- reactions: $\text{Na}_2\text{SO}_4 + \text{CaS} + 2\text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{CaSiO}_3 + \text{SO}_2 + \text{S}$ (865°C); $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S} + 2\text{SiO}_2 = 2\text{Na}_2\text{SiO}_3 + \text{SO}_2 + \text{S}$ (865°C).

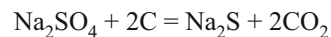
A eutectic appears in sulfate batch at the same temperature as in soda batch. However, when Na_2S appears it acts as a flux in the mixture $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S} + \text{SiO}_2$, the reaction starts at 500°C , and the onset temperature of the reaction $\text{Na}_2\text{SO}_4 + \text{SiO}_2$ decreases to $650 - 700^\circ\text{C}$.

The solid-phase reactions between the batch components already appear at 400°C and manifest in carbon encapsulation of sulfate grains [1]. The main sulfate – carbon reactions and the subsequent reaction of sulfate with the Na_2S and CaS formed and SO_2 and S release occur simultaneously at 500°C .

Sodium sulfate accelerates glassmaking and fining in two stages.

The **first stage** proceeds at $500 - 800^\circ\text{C}$ and is due to the formation of low-melting eutectics. However, the reduction of sodium sulfate does not proceed to complete decomposition. The final decomposition of sulfate with SO_2 and O_2 formation (**second stage**) occurs above 1400°C when the sulfate acts as a surface-active fining agent, which decreases the surface tension between the melt and gaseous inclusions.

According to the stoichiometric reaction



the reduction of one sodium sulfate molecule requires 24 g carbon, i.e., 16.9%. Under production conditions much less carbon is used for sodium sulfate reduction for colorless glass (6 – 10%). This amount of sodium sulfate is sufficient the function of sulfate at the first stage. The rest of the reducing agent is compensated by the reduction potential of the raw material, batch and redox conditions for glassmaking. If there is too little or too much reducing agent, difficulties appear in the technology.

The low amount of carbon compared with the stoichiometric reaction is due to the state of the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ equilibrium. To increase the visible-range light transmission of glass this equilibrium must be shifted rightward, i.e., to predominance of iron in the form Fe^{3+} . For heat-resistance characteristics of glass (decrease of IR transmission) the equilibrium must be shifted leftward (increase of diathermancy $\text{DT} = 10 - \tau_{1100} \text{ nm}$) [9].

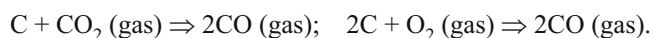
The SO_3 content in glass and a rightward shift of the iron equilibrium are indications of the acidification of the molten glass.

The absorption of SO_2 and SO_3 by the molten glass depends not only on its acid-base properties but also on the redox potential of the molten glass. The SO_3 content in glass decreases with increasing acidity, i.e., with increasing SiO_2 content. At the same time a decrease of SO_3 content in glass is related with the reducing conditions of S^{2-} formation, which is very characteristic for amber and brown container glasses.

When sulfates are used as fining agents in molten glass complex redox processes associated with the presence of several variable-valence elements, such as C, S and Fe, occur in it. When sodium sulfate is present in batch intermediate compounds are formed: CaSO_4 , Na_2CO_3 , $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, Na_2SO_3 , COS , Na_2S , CaS , $\text{Na}_2\text{Ca}(\text{SO}_4)_2$, SO_3 and S.

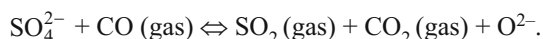
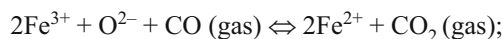
The correct choice of the amount of fining agent and the redox state of (ORS) of the molten glass and batch are important for high-quality fining. As batch heats up organic impurities present in the batch or cullet form carbon in part. In industrial production it has happened that the redox conditions of glassmaking sharply changed because of increased moisture content or settling of carbon on sand grains at the time the sand underwent heat-treatment in natural-gas-heated drum heaters. In this case, for stable sulfate/carbon ratio disruption of glassmaking can be disrupted because the diathermancy of the molten glass decreases and bottom layers of the molten glass, less enriched with oxygen, are drawn into the output flow. As a result the solubility equilibrium of gas in the glass is disrupted and fine seeds appear. As a rule the seeds contain SO_2 , since the sulfate-containing (oxidized) molten glass reacts with the sulfide-containing (reduced) molten glass and the oxygen diffusion coefficient is much larger than that of SO_2 . The equilibrium of the dissolved gases in the molten glass is disrupted, which causes bubbles to be released.

As batch melts carbon reacts with atmospheric carbon dioxide (CO_2 is formed as the carbonates in the batch decompose) or air oxygen (600 – 900°C). These reactions result in the formation of CO:



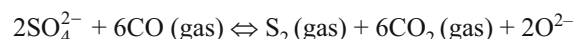
Subsequently, the reactions of the batch components with CO displace the equilibrium between the oxidized and reduced forms of the polyvalent elements in the direction of a more reduced state:

in weakly reduced batches:



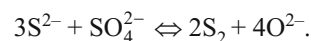
The glass becomes light-blue because of increased Fe^{2+} concentration:

in strongly reduced batches:



A yellowish-brown color can appear as a result of an iron-sulfide complex being formed.

The concentration levels of sulfide S^{2-} and sulfate SO_4^{2-} and the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ depend on the reduction potential of the molten glass. Sulfate and sulfide will react subsequently at temperatures 1000 – 1300°C via the reaction



In oxidized or weakly reduced molten glass part of the sulfate which has not reacted with CO during melting will decompose at temperatures > 1400°C: $\text{SO}_4^{2-} \Leftrightarrow \text{SO}_2 + \text{O}^{2-} + \frac{1}{2}\text{O}_2$.

These reactions continue until one component reacts completely.

Excess sulfate remains in oxidized or weakly reduced molten glass; excess sulfide remains under strongly reducing conditions.

The maximum solubility of SO_3 in molten glass is > 1% at 1000°C. For a sheet-glass furnace with a transverse flame on seven pairs of burners the maximum solubility of SO_3 was observed in the region of the first and second burner pairs and decreased to a minimum (0.4%) in the homogenization zone [10]. The solubility of SO_3 in molten glass is determined by the partial pressure of the oxygen dissolved in it.

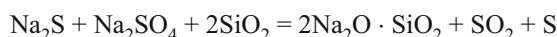
Thus, the sulfate/carbon ratio appears at the forefront of stabilization of the spectral characteristics of glass and technological processes but in combination with the ORP of batch and molten glass as well as the redox conditions of glassmaking. In addition, the oxygen content in the molten glass must be continually monitored (for example, with an oxygen sensor manufactured by the Kuhnreich-Meixner company).

In domestic glassmaking there is no experience in monitoring the oxygen partial pressure in commercial furnaces. As a result the real redox processes in glassmaking must be determined indirectly — by calculating the redox potential (ORP) of glass, determining the chemical oxygen demand (COD) of the raw materials and batch, monitoring excess air or oxygen during fuel combustion as well as the composition of the exhaust gases. The COD of the raw materials depending on their type and purity varies over a wide range [12].

This indirect approach through a determination of the COD of the raw materials and batch was proposed in 1978 by V. Manring and R. Davis and elaborated by German scientists (H. Jebesen-Marwedel and R. Brückner) and domestic scientists (Yu. A. Guloyan and N. A. Pankova). At present some questions concerning the need to take account of the COD of raw materials and batch have appeared, but experience has shown the efficacy of taking account of these indicators.

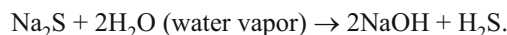
If the sulfate/carbon ratio taking account of the COD of raw materials and batch is not matched to the glassmaking conditions, then complete reduction and decomposition of sulfate may not be attained. Then, a layer of unfused Na_2SO_4 , in which CaSO_4 and Na_2SiO_3 are dissolved, remains on the surface of batch and molten glass. The formation of such a layer on the surface of silicate melt is explained by the poor solubility of sulfate in silicate melt, as a result of which liquation — the separation into two liquids — occurs. A Na_2SO_4 -rich layer lies at the top and a silica-enriched layer at the bottom. The excess reducing agent can lead to a sharp decrease of the diathermancy of the molten glass and its color as a result of the formation of chromophoric iron-sulfide complexes.

Sulfate is very soluble in cold and hot water. *Moisture* has a large effect on the course of the sulfate reduction reaction. In completely dry batch (sealed vessel) the components do not enter in an interaction; this process starts only in air open to water vapor. For this reason the equation



does not correspond to the actual process in moist batch [1].

A more likely process in moist *sulfate-containing batch* is



Sodium hydroxide easily enters into reaction with silica, since the melting temperature of NaOH is 328°C. Under production conditions moisture evaporates from the bottom layers of the batch, permeates the top melted film and hydrolyzes Na_2S to NaOH. The formation of NaOH requires two H_2O molecules per Na_2S molecule in the batch. N. A. Pankova's and our studies have shown that NaOH is not formed in moistened soda batch. For *soda batch* NaOH must be specially introduced into the batch in order to activate a chemical interaction [13, 14].

We have investigated the visible-range and IR transmission of domestically produced commercial glasses with different SO_3 content. We have shown that even though their light transmission is close in the visible range (85 – 90%) the glasses differ sharply with respect to the index $\text{DT} = 10^{-1} \tau_{1100} \text{ nm}$ and light transmission (45 – 70%); this is explained by the uncontrollable redox conditions of the technological process [9]. Despite some differences in the chemical composition of the glasses and, correspondingly, the acidity index (2.88 – 3.07), the main “indicator” of the molten glass ORP is the SO_3 content.

In the 1950s – 1970s there were not limits on the SO_3 content in sheet glass. It is shown in the works of N. A. Pankova and L. Ya. Levitin that the SO_3 content < 0.6% in glasses with VVS compositions and ranges from 0.6 to 0.8% in BVVS glass compositions.

It is now known that the SO_3 content must not exceed 0.4%. To increase visible-range transmission it is desirable to have acidic molten glass (higher SO_3 content), since the equilibrium $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ is displaced rightward; for heat-re-

sistant glass (lower SO_3 content) the Fe^{3+} content shifts leftward.

The fact that the molten glass can absorb sulfur gases from the atmosphere inside the furnace must be taken into account. The maximum absorption temperature is 1100°C. This temperature equals the temperature at the molten glass discharge into the float tank, whose protective atmosphere also contains sulfur compounds [15].

A mobile, temperature-dependent equilibrium exists between the gaseous sulfur compounds and the molten glass: when the melt is cooled the sulfur compounds separate from it and as a result the solubility decreases.

The molten glass entering production contains physically and chemically dissolved gases. Boiling of the molten glass with formation of *secondary* bubbles is observed on reheating. In order for 1000 bubbles with diameter 0.2 mm to form per kilogram of glass it is sufficient to have 1 cm³ of dissolved gas.

Thus, the main regulator of the spectral characteristics of glass and glassmaking processes are the ratios *sulfate – reducing agent – moisture – ORP (COD) of the batch and molten glass as well as the temperature and gas atmosphere during glassmaking*.

Adhering to GOST 6318–77 the domestic glass industry uses mainly chemically produced water-free sulfate, of which there are several sorts: highest, I, II and B (for the glass industry).

In 1990 we reviewed the alkali-containing byproducts — production wastes. At present many such materials are certified and used in various fields, for example, “Sodium: Sulfate, Technical,” TU 21-249-00204168–92; “Sodium: Sulfate, Natural (Purified),” TU 2141-084-00209527–99 and others.

Such products raise difficulties in technology. For example, when hydrosulfate replaces water-free sulfate or a production byproduct containing impurities such as NaCl, sulfides and so forth are used it is necessary to take account of the fact that NaCl content from 0.1 to 1% in batch has a large effect on processes occurring in batch.

The formation of soda crystal hydrates and their effect on the moisture content are well known. Sodium sulfate also forms the crystal hydrates $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite). The former loses water at 24.4°C and the latter at 32.4°C. For this reason the temperature interval recommended for moistening soda batch in terms of soda is 35.5 – 100°C (the optimal temperature is 60°C) and is probably also good for the dehydration of sodium sulfate.

Various types of carbon-containing materials (coal and charcoal) are used as reducing agents.

The solid-phase reduction of sulfate depends on the type of coal. Coal (D grade) decomposition and volatilization of its component parts were observed to start at 260°C. The coal mass loss before entry into reaction with Na_2SO_4 (500°C) is about 50%. Graphite (several brands) is recommended for decreasing burnup. Tests using different solid reducing

agents in batch established that electrode carbon is most resistant to burnup.

At the present time glass plants use mainly coals as reducing agents. For example, according to GOST R51586–2000 “Coals and anthracite from the Kuznetsk basin of the Itatskoe deposit” coals are divided according to grade and possess particles of different size and ash content, but special attention must be given to the fact that the moisture mass fraction can range from 10 to 40%. In addition, coals can be oxidized and reduced.

Modern technologies are automated and computerized. Parameters which are correlated with one another must be used to control them. Since plants operate on different raw material, the sulfate/carbon ratio combined with the COD of the raw material and batch will be *individual for each process line*.

For the most part commercial sheet and container glass process lines with a perfected sulfate/carbon ratio operate stably. Nonetheless, the light transmission of glass can change unexpectedly, seeds can appear, the uniformity of the molten glass can become degraded, and the glass diathermancy and strength can decrease. There can be many reasons for this, so that a thorough complex analysis is needed to find them. But one of the main reasons is a change in the redox conditions of glassmaking, which in turn are determined by the following:

- high impurity content in all types of raw materials, batch and cullet;
- quality of sodium sulfates with respect to impurities;
- quality of the reducing agent with respect to impurities, ash and moisture content and cullet;
- high moisture content of raw materials, batch and cullet;
- introduction of reduced cullet, for example, light-blue sheet cullet, into oxidized molten glass with high light transmission;
- appearance in batch of additional carbon and CO, for example, at the time sand is dried in a gas-flame furnace, during complete combustion of gas in a glassmaking furnace (analysis of the gas composition of exhaust gases is required; the CO and O₂ concentrations determine the character of the gas atmosphere in the furnace — oxidative O₂ > 2%, reductive CO = 0.3 – 0.4%, neutral CO = 0%).

The effect of the particle size of the sulfate and reducing agent on their interaction in batch has not been adequately studied.

In order to establish a rational sodium sulfate/reducing agent ratio under industrial conditions it is necessary to have the statistics of actual process-line parameters over a period of at least three months taking account of the raw materials and batch quality, the temperature–time and redox conditions of glassmaking as well as the glass quality. Data analysis will aid in adjusting the sodium sulfate/reducing agent ratio under industrial conditions taking account of all process parameters.

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